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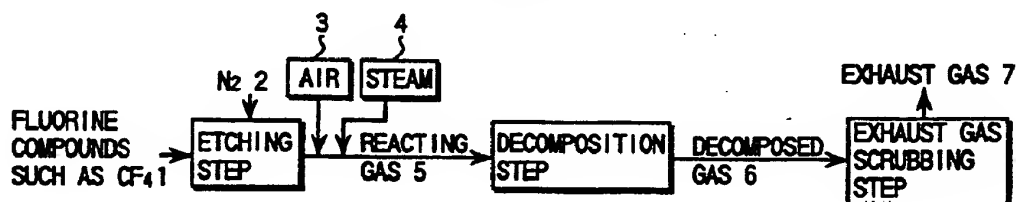
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(54) A treatment method for decomposing fluorine compounds, and catalyst and apparatus therefor

(57) A method of treatment for decomposing fluorine compounds, comprising the step of contacting a gas flow containing said fluorine compounds, which comprises fluorine as a halogen element, and any of the elements carbon, nitrogen, and sulphur as a compound with said fluorine, with a fluorine compound-decomposi-

tion catalyst in the presence of steam at a temperature in the range of approximately 200 to 800°C to hydrolyse the fluorine compound in said gas flow, wherein said gas flow containing said fluorine compounds is contacted with a catalyst comprising Al to convert said fluorine compounds to hydrogen fluoride.

FIG. 1



Description

BACKGROUND OF THE INVENTION

5 The present invention relates to a method of treatment for decomposing halogen compounds containing only fluorine as the halogen such as CF_4 , C_2F_6 , SF_6 , NF_3 , and the like at a low temperature effectively, and a catalyst and an apparatus therefor.

A large amount of halogen compound gas containing only fluorine as the halogen such as CF_4 , C_2F_6 , SF_6 , NF_3 , are used as a semiconductor etching agent, a semiconductor cleaner, and the like. However, it was found that these
10 compounds, once discharged into the atmosphere, turn into warming substances causing global warming.

Gases such as CF_4 , C_2F_6 , SF_6 , NF_3 , contain a large amount of fluorine (F) as one of molecular composing elements. Fluorine has the highest electronegativity among all the chemical elements, and forms chemically very stable compounds.

Particularly, CF_4 , C_2F_6 , and the like are substances having a strong intramolecular force, and a poor reactivity.
15 Based on the above property, when CF_4 is decomposed by combustion, heating up to a high temperature is required, and a remarkably large amount of energy is consumed.

Furthermore, a corrosion velocity of materials in the apparatus for the decomposition reaction at a high temperature by the generated gases such as hydrogen fluoride and the like is large, and no adequate method for decomposing treatment has been proposed yet at present.

20 One of the methods for decomposing treatment being proposed at present is technology for combustion at a high temperature. However, in accordance with the proposed method, a large amount of CO_2 and NO_x , i.e. hazardous substances, are generated by combustion, because combustible gases such as propane gas and the like are used. Due to use of flammable gases such as propane and the like, a danger of explosion is existed. Furthermore, due to combustion at approximately 1000°C , oven wall material is damaged by corrosive gases generated by the decomposition of halogen compounds, and an operation cost is increased because frequent maintenance is required. Accordingly, technology to decompose the halogen compounds at a low temperature without generating hazardous substance is necessary.

Although various applications regarding the catalysts for decomposing halogen compounds have been filed, any report on decomposition of halogen compounds containing only fluorine as the halogen has not been disclosed. Although a method for hydrolyzing halogen compounds with a catalyst comprising titania has been disclosed in JP-A-3-66388 (1991), it is described that the method does not indicate any decomposing performance for CF_4 , which contains only fluorine as the halogen. Okazaki et al intended to hydrolyze $\text{CFC-14}(\text{CF}_4)$ using Fe_2O_3 /active carbon, but the compound was not decomposed as described in Chem. Lett. (1989) pp. 1901-1904. Regarding the decomposition of halogen compounds containing only fluorine as the halogen, JP-A-7-116466 (1995) disclosed an example using a decomposing agent comprising an inorganic oxide treated with hydrogen fluoride.
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SUMMARY OF THE INVENTION

One of the objects of the present invention is to provide a method for treating fluorine compounds containing only fluorine as the halogen such as CF_4 , C_2F_6 , SF_6 , NF_3 , and the like to decompose at a low temperature effectively, catalysts having a high decomposition rate and a long catalytic life, and apparatus of the treatment for decomposition therefor.
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The inventors have achieved the present invention by proceeding an investigation in detail on a method for decomposition treatment, which is capable of decomposing compounds containing only fluorine as the halogen such as CF_4 , C_2F_6 , SF_6 , NF_3 , and the like at a low temperature with a high efficiency, and of suppressing corrosion of the apparatus caused by corrosive gases in the decomposed gas.
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The inventors found that a compound containing only fluorine as halogen, the compound is composed of the fluorine with any element selected from the group consisting of carbon, sulfur, and nitrogen, could be hydrolyzed and the fluorine compound in a gas flow could be converted to hydrogen fluoride by contacting the gas flow containing the fluorine compound with a catalyst comprising Al in the presence of steam at a temperature in the range of approximately
50 $200 - 800^\circ\text{C}$.

The object gas, i.e. a halogen compound containing only fluorine as the halogen such as CF_4 , C_2F_6 , and the like, has a strong intramolecular force based on the nature of fluorine having a high electronegativity, and a poor reactivity. The object gas is scarcely reacted and decomposed with oxygen, but it can be decomposed with a high decomposition rate by addition of H_2O .

55 The fluorine compounds, which are objects of the present invention, contain only fluorine as the halogen. Constituent elements of the compounds are fluorine, carbon, oxygen, sulfur, nitrogen, and the like. Examples of the compounds are CF_4 , CHF_3 , CH_2F_2 , CH_3F , C_2F_6 , C_2HF_5 , $\text{C}_2\text{H}_2\text{F}_4$, $\text{C}_2\text{H}_3\text{F}_3$, $\text{C}_2\text{H}_4\text{F}_2$, $\text{C}_2\text{H}_5\text{F}$, C_3F_8 , $\text{CH}_3\text{OCF}_2\text{CF}_3$, C_4F_8 , C_5F_8 , SF_6 , NF_3 , and the like.

The method of treatment for decomposing the fluorine compounds of the present invention uses a catalyst containing Al. The Al is used in a form of an oxide. Al can be used in both alone and as a complex with at least one component selected from the group consisting of Zn, Ni, Ti, Fe, Sn, Pt, Co, Zr, Ce, and Si. A decomposing activity of the catalyst can be enhanced by adding S to these catalysts.

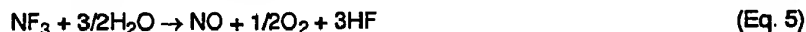
Necessary characteristics as catalytic performance are having a high decomposition rate and a long catalytic life. After investigating in detail of the catalyst having the above performance, it was found that a single body composed of only Al_2O_3 could have a high decomposition performance depending on its kind of raw material.

A higher decomposition rate can be obtained by using a catalyst, which contains at least one element selected from the group consisting of Zn, Ni, Ti, Fe, Sn, Pt, Co, Zr, Ce, and Si in addition to Al, than a case when only Al is used as the catalyst. In these catalyst, Al exists in a form of Al_2O_3 , or a complex oxide with the added metallic element. Any of Zn, Ni, Ti, Fe, Sn, Co, Zr, Ce, and Si exists in a form of an oxide, or a complex oxide with Al. In accordance with these catalyst, an atomic ratio of Al : M (where, M is at least one of Zn, Ni, Ti, Fe, Sn, Co, Zr, Ce, and Si) is desirably in the range of 50 - 99 mol % for Al, and 50 - 1 mol % for M. When the catalyst is composed of Al and Pt, the catalyst desirably contains Pt by 0.1 - 2 % by weight. A high decomposition rate can be obtained by selecting the amount of the additive component other than Al in the range indicated above.

In order to obtain a long catalytic life, suppressing crystallization of the Al_2O_3 in the catalyst is effective, and forming a complex oxide of Al such as NiAl_2O_4 , ZnAl_2O_4 , and the like by added metallic components such as Ni, Zr, and the like is desirable. As one of the methods for improving the catalytic performance, a method to add S to the catalyst is known. As a method for adding the S, various methods such as using a sulfuric acid salt, or sulfuric acid, when manufacturing the catalyst can be used. The S in the catalyst exists in a form of SO_4 ions and the like, and operates to enhance an acidic property of the catalyst. The amount of S is desirably in the range of 0.1 - 20 % by weight.

In accordance with the method of treatment for decomposition of the present invention, oxygen can be added into the gas flow containing the fluorine compound such as CF_4 , C_2F_6 , and the like. The oxygen can be used for an oxidation reaction of CO and the like in the decomposition gas.

Representative reactions of the fluorine compound decomposing reaction are as follows:



In accordance with the reactions expressed by the Eq. 1 and Eq. 2, Co is generated. However, the catalyst of the present invention has CO oxidizing performance, and if oxygen exists, CO can be oxidized to CO_2 .

The amount of added steam is required to be controlled so as to generate hydrogen atoms in an amount of at least equivalent to the number of F in the fluorine compound to be treated. Accordingly, fluorine in the compound can be converted to hydrogen fluoride, and a condition which facilitates post-treatment can be generated.

The reaction temperature for hydrolyzing the fluorine compound is desirably in the range of approximately 200 - 800 °C. The range of approximately 500 - 800 °C is desirable as the reaction temperature for treating the fluorine compound, which is composed of at least carbon, fluorine, and hydrogen. If a temperature higher than the above range is used, a higher decomposition rate can be achieved, but rapid deterioration of the catalyst is caused. Furthermore, the corrosion velocity of the apparatus material is increased rapidly. On the contrary, if a temperature lower than the above range is used, the decomposition rate is low.

When contacting the gas flow containing the fluorine compound, which contains only fluorine as the halogen, and any element selected from the group consisting of carbon, sulfur, and nitrogen, with the catalyst of the present invention, the content of the fluorine compound in the gas flow is desirably in the range of 0.1 - 10 % by volume, and preferably 0.1 - 3 % by volume. The space velocity is desirably in the range of 100 per hour - 10,000 per hour, and preferably 100 per hour - 3,000 per hour. Where, the space velocity is defined by the following equation.

$$\text{Space velocity (h}^{-1}\text{)} = \text{Flow rate of the reacting gas (ml/h) / the amount of catalyst (ml)}$$

In accordance with the method of treatment for decomposing fluorine compounds of the present invention, hydrogen fluoride, carbon dioxide, and the others are generated as decomposition products. Additionally, sulfur oxides such as SO_2 , SO_3 , and the like, and nitrogen oxides such as NO, NO_2 , and the like, are generated in some cases. In order

to neutralize and eliminate these products, a method of scrubbing the decomposed gas by spraying an aqueous alkaline solution is desirable, because blocking of the pipe with precipitated crystal can be hardly occurred. Any one of other methods of bubbling the decomposed gas into an alkaline solution, and of scrubbing the decomposed gas using a packed column can be used. Alkaline solid bodies can also be used. As the alkaline material, any of aqueous solution or slurry of calcium hydroxide, sodium hydroxide, and conventional alkaline reagents can be used.

As a raw material of Al for manufacturing the catalyst of the present invention, any of γ -alumina, a mixture of γ -alumina and δ -alumina, and the like can be used. Particularly, a catalyst manufactured by using boehmite as the raw material for Al, and forming the oxide by calcining has a high decomposition activity.

As raw materials of various metallic components for manufacturing the catalyst of the present invention, nitrate, sulfate, ammonium salt, chloride, and the like of the metals can be used. Nickel nitrate, nickel sulfate, and the like can be used as a raw material of Ni. Hydrates of these compounds can be used. Titanium sulfate, titania sol, and the like can be used as raw materials of Ti.

Any of the conventional methods for manufacturing catalyst such as precipitation method, impregnation method, kneading method, and the like, can be used for manufacturing the catalyst of the present invention.

The catalyst of the present invention can be used by forming a shape of granule, honey-comb, and the like. Any of extrusion method, pelletizing method, roller granulating method, and the like can be used arbitrarily depending on the object. The catalyst of the present invention can also be used by being coated onto a honeycomb, a plate, or the like, which are made of ceramics or metal.

Any of conventional fixed bed, moving bed, or fluidized bed can be used as a reactor for performing the method of the present invention. However, because corrosive gases such as HF and the like are generated as the decomposition gas, the reactor must be composed of materials, which are corrosion resistance against these corrosive gases.

The treating apparatus for performing the method of the present invention comprises: in addition to the above reactor, means for controlling the concentration of the fluorine compound in the gas flow, for instance, means for supplying nitrogen, air, or oxygen to the gas flow, means for heating at least one of the gas flow and the catalyst in order to contact them each other at a temperature in the range of 200 - 800 °C, means for adding steam for decomposing the fluorine compound to the gas flow, and an exhaust gas scrubber for neutralizing a part of carbon dioxide, a part of sulfur oxides such as SO₂, SO₃, and the like, and a part of nitrogen oxides such as NO, NO₂, and hydrogen fluoride in the decomposition products by scrubbing the decomposition products, which have been generated by contacting the gas flow with the catalyst filled in the reactor, with an alkaline solution. Furthermore, means for adsorbing carbon monoxide, sulfur oxide, nitrogen oxide, which have not been absorbed by alkaline scrubbing, by an adsorbent, and the like, is preferably provided at a rear step of the exhaust gas scrubber.

The method of treatment for decomposing the gas containing fluorine compounds of the present invention can be applied to previously installed semiconductor plants. The semiconductor plant has generally an exhaust gas treating apparatus for acidic component gas. The fluorine compound can be decomposed by utilizing the exhaust gas treating apparatus by the steps of: providing only the catalyst of the present invention into the exhaust gas line for the fluorine compound such as CF₄, adding steam, and heating the gas flow.

In accordance with the present invention, the whole apparatus, or a part of the apparatus of the present invention is loaded onto a truck and the like, the truck moves to the place where the cylinder containing the fluorine compound is stored, the fluorine compound is taken out from the cylinder, and the fluorine compound taken out from the cylinder can be treated directly by the apparatus of the present invention. A circulating pump for circulating the scrubbing solution in the exhaust gas scrubber, and the exhaust gas adsorption column for adsorbing gases such as carbon monoxide in the exhaust gas can be loaded simultaneously. Furthermore, a generator can be loaded.

The method of treatment for decomposing the fluorine compound of the present invention can decompose the halogen compound at a lower temperature, and accordingly, the operation cost can be reduced.

When the gas containing fluorine compound is treated, corrosion of the apparatus materials by acidic components such as HF, which are generated by the decomposition is a problem to be solved. However, in accordance with the present invention, the corrosion velocity is slow due to the low operating temperature. Therefore, the frequency of necessary maintenance of the apparatus can be reduced.

The method of treatment for decomposing the fluorine compound of the present invention comprises a catalytic reaction step for decomposing the fluorine compound, and an exhaust gas scrubbing step for neutralizing and eliminating the acidic component in the gas generated by the decomposition. Therefore, size of the apparatus can be reduced.

Because the decomposition reaction of the fluorine compound is with steam, the method of treatment for decomposing the fluorine compounds is highly safe, and danger for explosion, which will be encountered when combustible gas is used, can be eliminated.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow sheet indicating the treating process of embodiment 1 of the present invention,

FIG. 2 is a graph indicating performance of respective of the catalysts of the present invention,
 FIG. 3 is a graph indicating performance of respective of the catalysts of the present invention,
 FIG. 4 is a graph indicating performance of respective of the catalysts of the present invention,
 FIG. 5 is a graph indicating performance of respective of the catalysts of the present invention, and
 FIG. 6 is a graph indicating performance of respective of the catalysts of the present invention,
 FIG. 7 is a graph indicating results of decomposition reactions of SF_6 , and C_3F_8 ,
 FIG. 8 is a graph indicating results of decomposition reactions of CF_4 , C_4F_8 , and CHF_3 , and
 FIG. 9 is a schematic illustration indicating an example of the apparatus for treating fluorine compound of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, the present invention is explained in details with preferred embodiments. The present invention is not restricted to only the embodiments.

FIG. 1 indicates an example of a flow sheet of the treating process for decomposing halogen compounds used in a semiconductor etching process.

In accordance with the etching process, a halogen compound 1 such as CF_4 , and the like, is charged into a reduced pressure etching chamber, excited with plasma for 20 minutes, and reacted with semiconductors. Subsequently, the atmosphere in the chamber is replaced with N_2 2 to dilute the concentration of the halogen compound to a few %, and released as an exhaust gas by a velocity of approximately 10 liter/min.

Air was added by the gas adder 3 to the exhaust gas to dilute the fluorine compound such as CF_4 , and the like. At this time, nitrogen can be added to dilute the fluorine compound. Furthermore, both nitrogen and oxygen can be added to dilute the fluorine compound. A reacting gas 5, which is obtained by adding steam by the steam adder 4 to the diluted exhaust gas, is transferred to the decomposition step. The decomposition step is performed at the reactor filled with catalyst. The concentration of the fluorine compound in the reacting gas is approximately 0.5 - 1 %.

In the decomposition step, the reacting gas is contacted with a catalyst comprising Al at a temperature in the range of approximately 200 - 800 °C under a condition of space velocity 1,000 per hour (where, space velocity (h^{-1}) = flow rate of reacting gas (ml/h) / the amount of catalyst (ml)). In this case, the reacting gas may be heated, or the catalyst may be heated by an electric oven and the like. The decomposed gas 6 is transferred to the exhaust gas scrubbing step. In the exhaust gas scrubbing step, an alkaline solution is sprayed in the decomposed gas 6, and an exhaust gas 7, which is obtained by eliminating acidic components in the decomposed gas, is released to outside the treating system. The decomposition rate of the halogen compound such as CF_4 , and the like is obtained by analyzing the reacting gas 5 and the exhaust gas 7 with FID (Flame Ionization Detector) gas chromatography, and TCD (Thermal Conductivity Detector) gas chromatography, and calculating mass balances at inlet and outlet of the treating system.

FIG. 9 is a schematic illustration indicating an example of the treating apparatus of the present invention. The reactor 8 is filled with catalyst 9 comprising Al, and the whole body of the reactor can be heated by the heater 10. At a rear stage of the reactor 8, the exhaust gas scrubber 11 having means for spraying 12 an aqueous alkali solution is provided.

(Embodiment 1)

The present embodiment is an example of studying the activities of various fluorine compound decomposing catalysts.

Air was added to C_2H_6 gas of at least 99 % pure to dilute the gas. Steam was further added to the diluted gas. The steam was obtained by supplying pure water to upper portion of a reactor with a microtube pump by approximately 0.2 ml/min. and gasifying the pure water. The concentration of C_2H_6 in reacting gas was approximately 0.5 %. The reacting gas was contacted with a catalyst, which had been heated at a designated temperature from outside the reactor by an electric oven, under a space velocity of 2,000 per hour.

The reactor was a reacting tube made of Inconel, of which inner diameter was 32 mm, having a catalyst layer at the middle portion of the reactor. A thermocouple protecting sheath made of Inconel, of which outer diameter was 3 mm, was provided in the catalyst layer. The decomposition generated gas passed through the catalyst layer was bubbled into a calcium fluoride aqueous solution, and subsequently, released outside the system. The decomposition rate of C_2H_6 was calculated from the analytical result of FID gas chromatography and TCD gas chromatography by the following equation (math. 1).

$$\text{Decomposition rate} = 1 - (\text{amount of halogen compound at outlet} / \text{amount of supplied halogen compound}) \times 100 (\%) \quad (\text{math. 1})$$

Hereinafter, methods for preparing respective of catalyst examined in the present embodiment under the above

condition are explained.

Catalyst 1;

Commercial boehmite powder was dried at 120 °C for 2 hours. The dried powder 200 g was calcined at 300 °C for 0.5 hour, and subsequently, the calcining temperature was raised to 700 °C and calcined for 2 hours. The obtained powder was filled into a die, and fabricated by pressurizing with a pressure 500 kgf/cm². The fabricated bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst after finishing the above treatment was mainly composed of Al₂O₃.

Catalyst 2;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 85.38 g of zinc nitrate hexahydrate was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Zn = 91 : 9 (mol%) by an atomic ratio. The present catalyst contains a complex oxide of ZnAl₂O₄ in addition to Al oxides and Zn oxides.

Catalyst 3;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 50.99 g of nickel sulfate hexahydrate was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Ni = 91 : 9 (mol%) by an atomic ratio. The present catalyst contains Al oxides, Ni oxides, a complex oxide of NiAl₂O₄, and S oxides.

Catalyst 4;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 125.04 g of nickel nitrate hexahydrate was added to 300 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Ni = 91 : 9 (mol%) by an atomic ratio. The present catalyst contains Al oxides, Ni oxides, and a complex oxide of NiAl₂O₄.

Catalyst 5;

Commercial boehmite powder was dried at 120 °C for 1 hour. The dried powder 300 g and a 30 % titanium sulfate aqueous solution 354.4 g were mixed and kneaded with adding approximately 300 g of pure water. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 5 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Ti = 91 : 9 (mol%) by an atomic ratio.

Catalyst 6;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 115.95 g of iron nitrate hexahydrate was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Fe = 91 : 9 (mol%) by an atomic ratio.

Catalyst 7;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 95.43 g of stannic chloride hydrate was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Sn = 91 : 9 (mol%) by an atomic ratio.

Catalyst 8;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution obtained by diluting 22.2 g of dinitrodiamine Pt (II) nitric acid solution (Pt concentration was 4.5 % by weight) with 200 ml of pure water was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst after finishing the above treatment contained Pt by 0.68 % by weight to 100 % by weight of Al₂O₃.

Catalyst 9;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 125.87 g of cobalt nitrate hexahydrate was added to 300 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Co = 91 : 9 (mol%) by an atomic ratio.

Catalyst 10;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 76.70 g of zirconyl nitrate dihydrate was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Zr = 91 : 9 (mol%) by an atomic ratio.

Catalyst 11;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 124.62 g of cerium nitrate hexahydrate was added to 300 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Ce = 91 : 9 (mol%) by an atomic ratio.

Catalyst 12;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 129.19 g of 20% silica sol was added to 300 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Si = 91 : 9 (mol%) by an atomic ratio.

Results of the examination of the above catalysts 1 - 12 at a reacting temperature of 700 °C are indicated in FIG. 2. The decomposition rates by the catalyst comprising Al and Zn, and the catalyst comprising Al and Ni are significantly higher than others, and the decomposition rate of the catalyst comprising Al and Ti is next high. The reason that the catalyst 3 has a higher activity than the catalyst 4 is supposedly based on the effect of S.

(Embodiment 2)

The present embodiment is a result of examination on activities of catalysts by preparing catalysts, which were obtained by varying the composition of Al and Ni using the same raw materials of Al and Ni as the catalyst 4, in the embodiment 1, and determining their decomposition activities for C_2F_6 .

Catalyst 4 - 1;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 8.52 g of nickel nitrate hexahydrate was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Ni = 99 : 1 (mol%) by an atomic ratio.

Catalyst 4 - 2;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 66.59 g of nickel nitrate hexahydrate was added to 300 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Ni = 95 : 5 (mol%) by an atomic ratio.

Catalyst 4 - 3;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 210.82 g of nickel nitrate hexahydrate was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Ni = 80 : 20 (mol%) by an atomic ratio.

Catalyst 4 - 4;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 361.16 g of nickel nitrate hexahydrate was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Ni = 70 : 30 (mol%) by an atomic ratio.

Catalyst 4 - 5;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 562.1 g of nickel nitrate hexahydrate was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Ni = 60 : 40 (mol%) by an atomic ratio.

The activities of the above catalysts from the catalyst 4, the catalyst 4 - 1 to the catalyst 4 - 5 were examined by the same method as the embodiment 1 except changing the concentration of C_2F_6 to 2 %, and the supplying amount of the pure water to approximately 0.4 ml/min. The decomposition rates at 6 hours elapsed after initiating the examination are indicated in FIG. 3. The highest activity can be obtained when the mol % of Ni/(Ni+Al) is in the range of 20 - 30 mol %, and the activity is next high when the mol % is in the range of 5 - 40 mol %.

(Embodiment 3)

The present embodiment is a result of examination on activities of catalysts by preparing catalysts, which were obtained by varying the composition of Al and Zn using the same raw materials of Al and Zn as the catalyst 2 in the embodiment 1, and determining their activities.

Catalyst 2 - 1;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 215.68 g of zinc nitrate hexahydrate was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Zn = 80 : 20 (mol%) by an atomic ratio.

Catalyst 2 - 2;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 369.48 g of zinc nitrate hexahydrate was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Zn = 70 : 30 (mol%) by an atomic ratio.

Catalyst 2 - 3;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 96.39 g of zinc nitrate hexahydrate was added to 126.65 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Zn = 85 : 15 (mol%) by an atomic ratio.

The activities of the above catalysts from the catalyst 2, the catalyst 2 - 1 to the catalyst 2 - 3 were examined by the same method as the embodiment 1 except changing the concentration of C_2F_6 to 2%, and the supplying amount of the pure water to approximately 0.4 ml/min. The decomposition rates at 6 hours elapsed after initiating the examination are indicated in FIG. 4. The highest decomposition rate can be obtained when the mol % of Zn/(Zn+Al) is in the range of 10 - 30 mol %.

(Embodiment 4)

The present embodiment is a result obtained by performing decomposition of CF_4 , CHF_3 , and C_2F_6 at various reaction temperatures. The condition of the examination was as same as the embodiment 1, except changing the space velocity to 1,000 per hour, and the halogen compound was diluted with nitrogen instead of air. The catalyst used was the catalyst 4 - 3 in the embodiment 2. The results of the examination at various reacting temperature are indicated in FIG. 5. The catalyst comprising Al and Ni has a high decomposition rate with CF_4 , and CHF_3 . These catalyst also have a high activity with the fluorine compounds at a low temperature such as approximately 600 °C.

(Embodiment 5)

The present embodiment is a result obtained by examining the effect of steam in the decomposition of C_2F_6 . The condition of the examination was as same as the embodiment 1, except changing only the space velocity to 1,000 per hour. The catalyst used was the catalyst 4 in the embodiment 1, and the reacting temperature was 700 °C. In the examination, steam was supplied for 2 hours from the initiation of the reaction, and then, steam supply was stopped. After 5 hours elapsed, the steam supply was resumed. The results of the examination are indicated in FIG. 6. It was revealed that the decomposition rate was increased by adding steam, and the decomposition of C_2F_6 was performed by hydrolysis.

(Embodiment 6)

The present embodiment is a result obtained by examining the decomposition of SF_6 and C_3F_8 using the catalyst 4 - 3 comprising Al and Ni. The condition of the examination of SF_6 gas was as same as the embodiment 1, except using SF_6 of at least 99 % pure, changing the space velocity to 1,000 per hour, and diluting the SF_6 with nitrogen instead of air. The condition of the examination of C_3F_8 was as same as the embodiment 1. Results of the examination is indicated in FIG. 7. The decomposition rate was obtained by determining the amount of SF_6 in the reacting gas at the inlet of the reactor, and the amount of SF_6 in the decomposed gas after passing through the alkaline scrubber with the TCD gaschromatography, and calculating the decomposition rate by the following equation (math. 2). The observed decomposition rate of SF_6 at the reacting temperature 550 - 700 °C was at least 99 %. In accordance with the decomposition test of C_3F_8 , a high decomposition rate could be obtained at a reacting temperature higher than 700 °C.

$$\text{Decomposition rate} = 1 - (\text{amount of } \text{SF}_6 \text{ at the outlet} / \text{amount of supplied } \text{SF}_6) \times 100 (\%) \quad (\text{math. 2})$$

(Embodiment 7)

The present embodiment is a result obtained by examining the decomposition of NF_3 using the catalyst 4 - 3 comprising Al and Ni. The condition of the examination was as same as the embodiment 6, except using NF_3 of at least 99 % pure. The reacting temperature was 700 °C. The decomposition rate was obtained by determining the amount of NF_3 in the reacting gas at the inlet of the reactor, and the amount of NF_3 in the decomposed gas after passing through the alkaline scrubber with the TCD gaschromatography, and calculating the decomposition rate by the following equation (math. 3). The observed decomposition rate was at least 99 %.

$$\text{Decomposition rate} = 1 - (\text{amount of } \text{NF}_3 \text{ at the outlet} / \text{amount of supplied } \text{NF}_3) \times 100 (\%) \quad (\text{math. 3})$$

(Embodiment 8)

The decomposition of CF_4 , C_4F_8 , and CHF_3 were examined using the catalyst comprising Al and Zn in an atomic ratio of Al:Zn = 85:15 (mol %).

The decomposition of CF_4 was examined by the steps of diluting CF_4 gas of purity at least 99 % by adding air, further adding steam, and contacting with the catalyst at a designated reacting temperature. The space velocity was 1000 per hour.

The CF_4 concentration in the reacting gas was approximately 0.5 %. The flow rate of the steam was controlled to be approximately 50 times of the CF_4 gas. The decomposition of CHF_3 and C_4F_8 were performed by the same as the above.

Results of the examination are indicated in FIG. 8. It was revealed that the catalyst comprising Al and Zn had a high activity with CHF_3 and CF_4 , and the catalyst indicated a high decomposition activity with C_4F_8 when the reacting temperature was increased to approximately 700 °C or higher.

In accordance with the present invention, halogen compounds which contain only fluorine as the halogen such as CF_4 , C_2F_6 , and the like can be treated for decomposing effectively.

Claims

1. A method of treatment for decomposing fluorine compounds, comprising the step of contacting a gas flow containing said fluorine compounds, which comprises fluorine as a halogen element, and any of the elements carbon, nitrogen, and sulphur as a compound with said fluorine, with a fluorine compound-decomposition catalyst in the presence of steam at a temperature in the range of approximately 200 to 800 °C to hydrolyse the fluorine compound in said gas flow, wherein said gas flow containing said fluorine compounds is contacted with a catalyst comprising Al to convert said fluorine compounds to hydrogen fluoride.
2. The method of claim 1, wherein said gas flow containing fluorine compounds contains at least one fluorine compound selected from CF_4 , CHF_3 , C_2F_6 , C_3F_8 , C_4F_8 , and C_5F_8 , and said fluorine compound is decomposed to at least either one of CO and CO_2 , and HF.
3. The method of claim 1, wherein said gas flow containing fluorine compounds contains SF_6 as said fluorine compound, and said SF_6 is decomposed to at least either one of SO_2 and SO_3 , and HF.
4. The method of claim 1, wherein said gas flow containing fluorine compounds contains NF_3 as said fluorine com-

pound, and said NF_3 is decomposed to at least either one of NO and NO_2 , and HF.

- 5 5. The method any preceding claim, wherein said gas flow containing said hydrogen fluoride, after contacting with the catalyst, is neutralised by scrubbing with an aqueous alkali solution.

6. A catalyst for decomposing fluorine compounds containing an Al oxide, which is used for hydrolysing halogen compounds containing only fluorine as the halogen.

- 10 7. The method of any of claims 1 to 5 or the catalyst of claim 6, wherein said catalyst contains Al, at least one of the elements Zn, Ni, Ti, Fe, Sn, Co, Zr, Ce, Si, and Pt, the atomic ratio of Al : M (where, M is any one of Zn, Ni, Ti, Fe, Sn, Co, Zr, Ce and Si) being preferably 50 to 99 mol % for Al and 50 to 1 mol % for M.

8. The method or catalyst of claim 7, wherein said catalyst further contains S, preferably in the range of 0.1 to 20 % by weight.

- 15 9. The method or catalyst of claim 7 or 8, wherein respective of components comprising said catalyst is contained in any form of an oxide of the component alone, and a complex oxide of Al with other components.

- 20 10. The method or catalyst of any of claims 7 to 9, wherein said catalyst contains Al and 0.1 to 2 % by weight of Pt.

11. A treating apparatus for decomposing fluorine compounds comprising

a reactor filled with catalyst for decomposing fluorine compounds,

25 a gas adder to generate a gas flow containing a compound, which is composed of fluorine and any one of carbon, sulphur, and nitrogen, by adding any of nitrogen, oxygen, and air to said fluorine compounds, which is introduced into said reactor,

a heater for heating at least any one of said catalyst filled in said reactor and said gas flow supplied to said reactor to a temperature in the range of approximately 200 to 800 °C, and

30 a steam adder for adding steam for hydrolysing said fluorine compounds to said gas flow,

wherein said reactor is filled with a catalyst comprising Al.

12. The apparatus of claim 11, wherein an exhaust gas scrubber for scrubbing said gas flow discharged from said reactor with an aqueous alkali solution is provided at a rear stage of said reactor.

FIG. 1

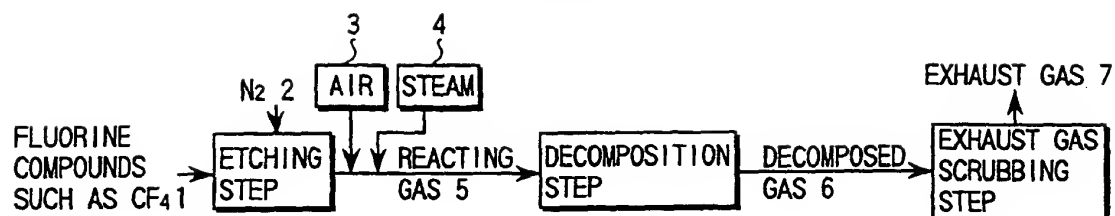


FIG. 2

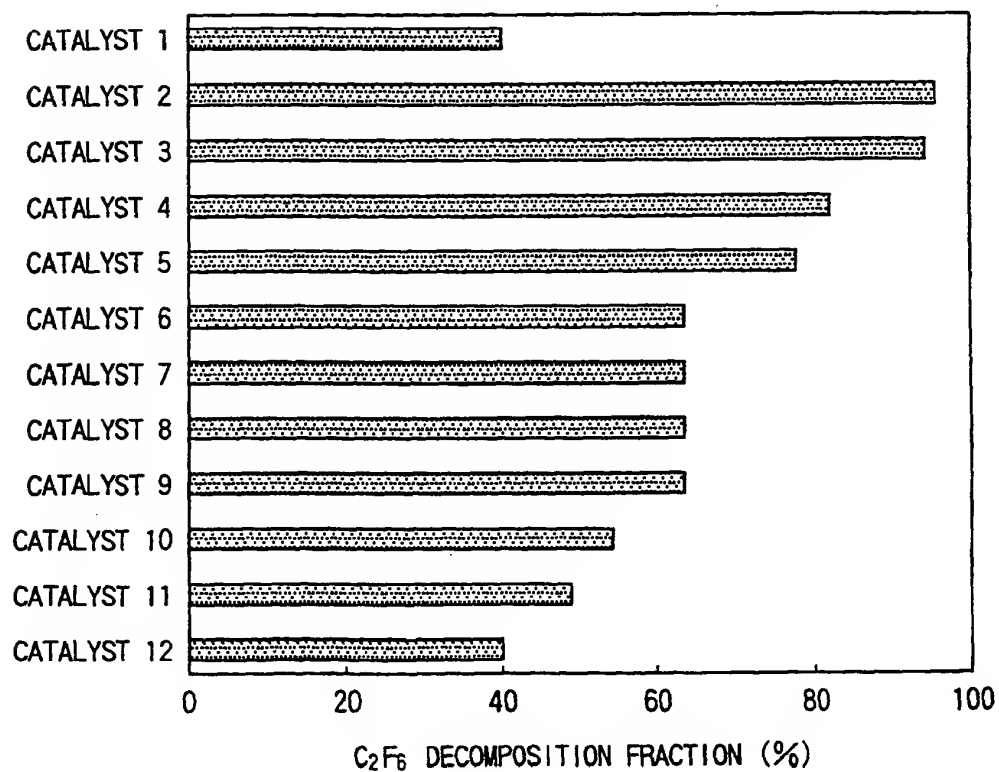


FIG.3

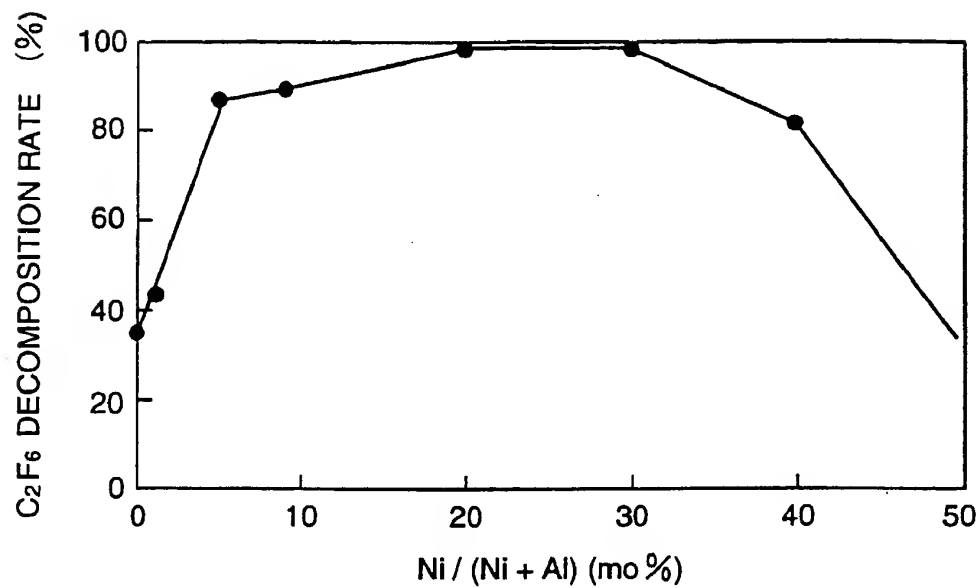


FIG.4

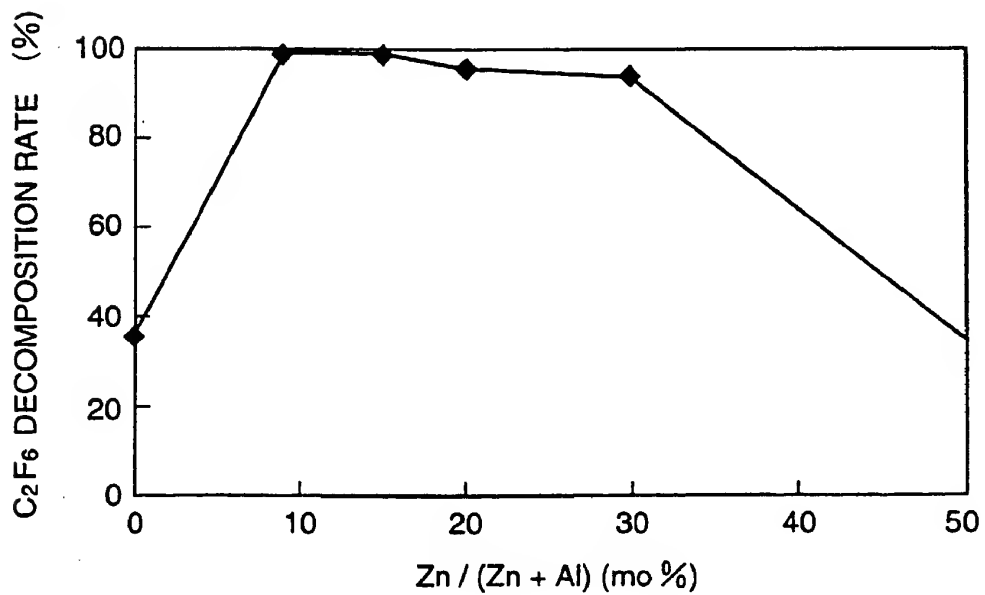


FIG.5

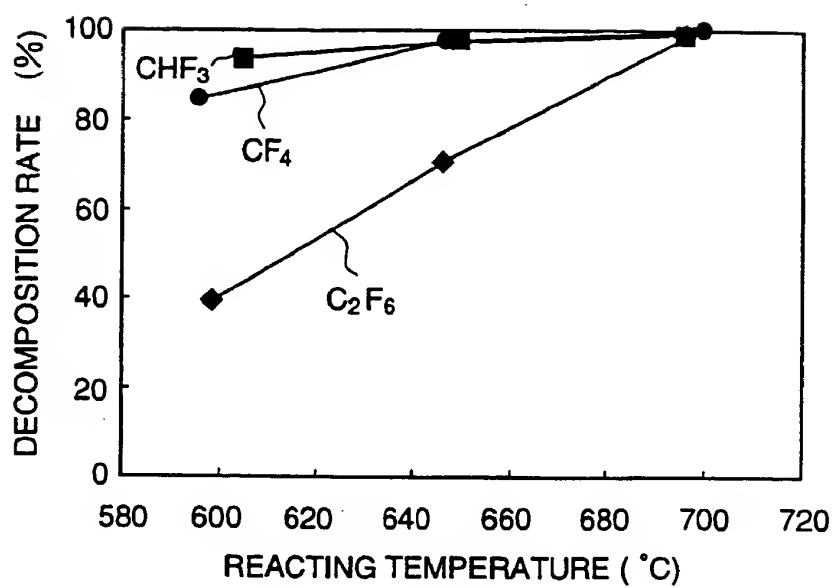


FIG.6

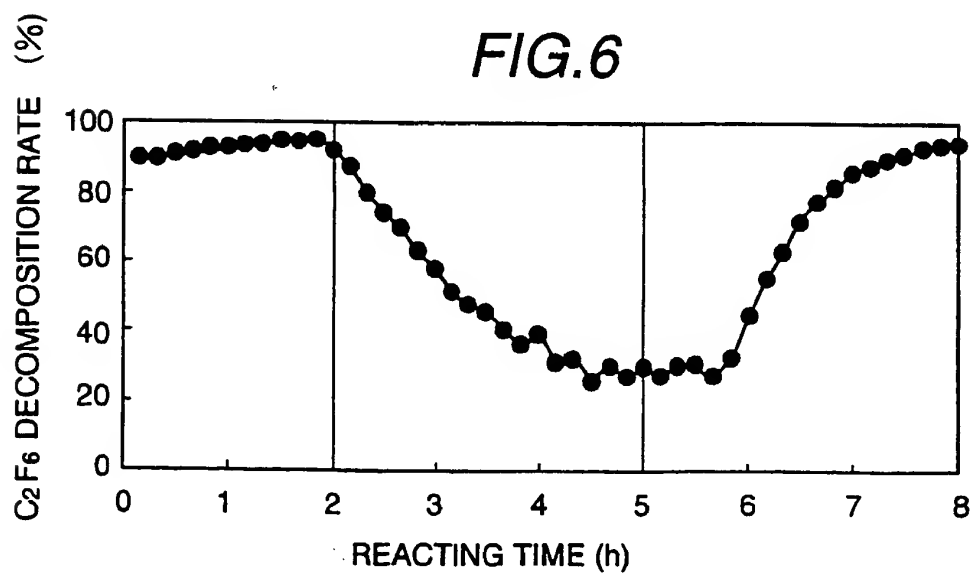


FIG.7

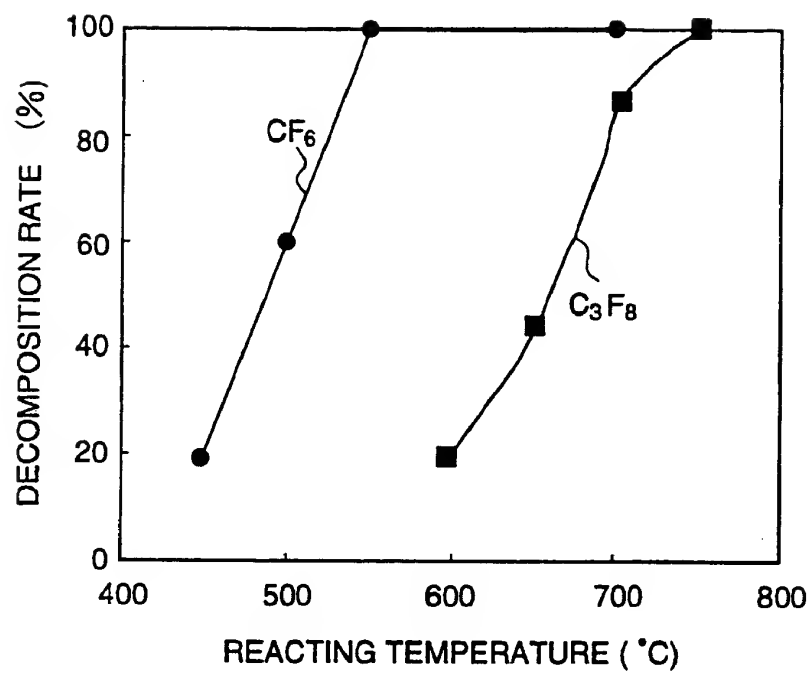


FIG.8

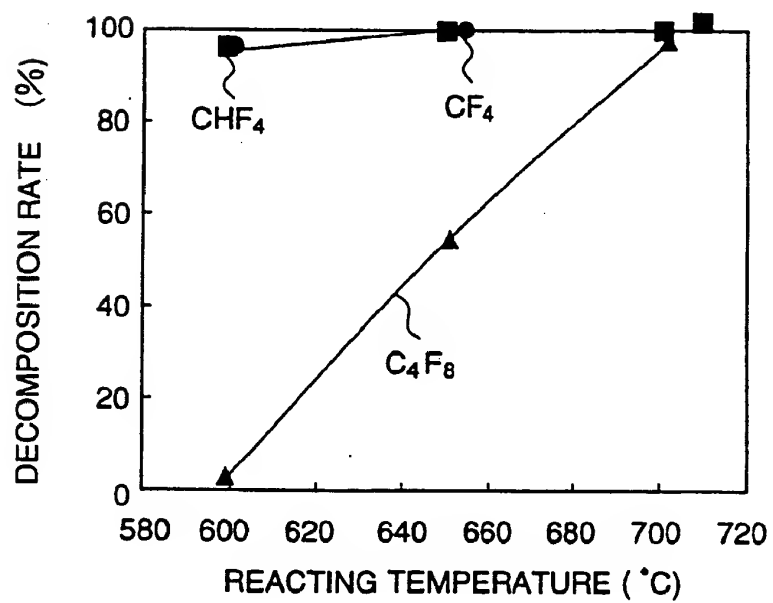
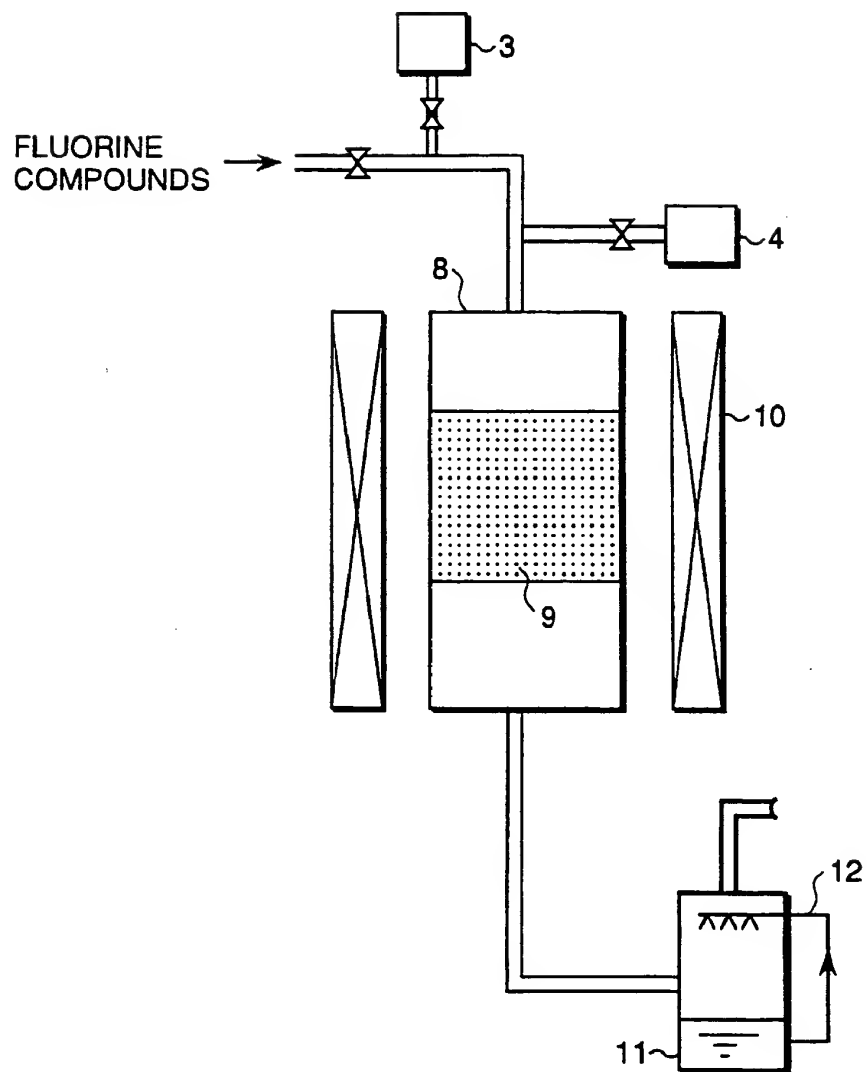


FIG.9





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 11 0080

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P,X	WO 97 49479 A (CS HALBLEITER SOLARTECH) 31 December 1997 * page 4, paragraph 1 - page 5, paragraph 1 * * page 7, paragraph 2 - paragraph 4 * * page 9, paragraph 1 * * page 14, paragraph 3 * ---	1-4,6,7,9	B01D53/86 A62D3/00
X	EP 0 642 809 A (CHEMIE LINZ GMBH) 15 March 1995 * page 1, line 27 - page 51 * * page 2, line 28 - line 57; example 1 * ---	1,2,5-7,9,11,12	
X	DE 43 11 061 A (SOLVAY FLUOR & DERIVATE) 6 October 1994 * the whole document * ---	1,4,6	
X	DATABASE WPI Section Ch, Week 8802 Derwent Publications Ltd., London, GB; Class E36, AN 88-010405 XP002078730 & JP 62 273 039 A (KANTO DENKA KOGYO KK) * abstract * ---	1,4,6,7	TECHNICAL FIELDS SEARCHED (Int.Cl.6) B01D A62D
X	EP 0 597 393 A (JAPAN PIONICS) 18 May 1994 * claims; table 7 * ---	1,4,6,7	
X,D	EP 0 412 456 A (MITSUI DU PONT FLUORCHEMICAL) 13 February 1991 * page 3, line 12 - page 4, line 37; examples * -----	1,5-7,9,11,12	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 25 September 1998	Examiner Eijkenboom, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document</p>			

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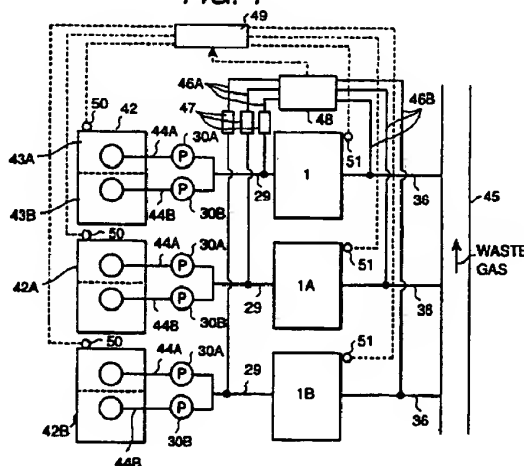
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(54) A method for processing perfluorocarbon and an apparatus therefor

(57) An exhaust gas containing a perfluoride compound (PFC) and SiF_4 is conducted into a silicon remover and contacted with water. A reaction water supplied from a water supplying piping and air supplied from an air supplying piping are mixed with the exhaust gas exhausted from the silicon remover. The exhaust gas containing water, air, and CF_4 is heated at 700°C by a heater. The exhaust gas containing PFC is conducted to a catalyst layer filled with an alumina group catalyst. The PFC is decomposed to HF and CO_2 by the catalyst. The exhaust gas containing HF and CO_2 at a high temperature exhausted from the catalyst layer is cooled in a cooling apparatus. Subsequently, the exhaust gas is conducted to an acidic gas removing apparatus to remove HF. In accordance with the present invention, the silicon component is removed from the exhaust gas before introducing the exhaust gas into the catalyst layer. Therefore, surface of the catalyst can be utilized effectively, and the decomposition reaction of the perfluoride compound can be improved.

FIG. 1





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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
E	EP 0 885 648 A (HITACHI LTD) 23 December 1998 (1998-12-23) * page 2, line 46 - line 50 * * page 3, line 55 - page 4, line 5; claim 1 *	1,3,4, 9-11,13, 25,26	B01D53/86 B01D53/14 H01L21/00
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 119 (C-579), 23 March 1989 (1989-03-23) & JP 63 291625 A (TOYO SANSO KK), 29 November 1988 (1988-11-29) * abstract *	1,11,25	
A	US 5 649 985 A (IMAMURA HIROSHI) 22 July 1997 (1997-07-22) * column 6, line 45 - line 51; claim 1 * * column 2, line 39 - line 43 *	1,11,25, 26	
A	EP 0 642 809 A (CHEMIE LINZ GMBH) 15 March 1995 (1995-03-15) * page 1, line 27 - line 32 *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B01D H01L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 October 1999	Examiner Faria, C
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 30 9136

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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14-10-1999

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0885648	A	23-12-1998	JP	11070322 A	16-03-1999
JP 63291625	A	29-11-1988	NONE		
US 5649985	A	22-07-1997	US	5716428 A	10-02-1998
EP 0642809	A	15-03-1995	AT	404431 B	25-11-1998
			AT	181993 A	15-04-1998
			US	5710359 A	20-01-1998

